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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08G 63/08, 63/88, C08L 67/04, C08J 5/18, C08K 5/14</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/18169</b> <b>(43) International Publication Date:</b> 6 July 1995 (06.07.95)
<b>(21) International Application Number:</b> PCT/FI94/00586 <b>(22) International Filing Date:</b> 29 December 1994 (29.12.94) <b>(30) Priority Data:</b> 935964 31 December 1993 (31.12.93) FI 945264 9 November 1994 (09.11.94) FI <b>(71) Applicant (for all designated States except US):</b> NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SÖDERGÅRD, Anders [FI/FI]; Käpytie 2 D 99, FIN-20810 Turku (FI). SELIN, Johan-Fredrik [FI/FI]; Isonmastontie 15 D, FIN-00980 Helsinki (FI). NIEMI, Maria [FI/FI]; Minna Canthinkatu 24 A 25, FIN-00250 Helsinki (FI). JOHANSSON, Carl-Johan [FI/FI]; Wadenströminkuja 32, FIN-06100 Porvoo (FI). MEINANDER, Kerstin [FI/FI]; Tikantie 6, FIN-06100 Porvoo (FI). <b>(74) Agent:</b> NESTE OY; Patent Services, P.O. Box 310, FIN-06101 Porvoo (FI).			<b>(81) Designated States:</b> JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESSABLE POLY(HYDROXY ACIDS)			
<b>(57) Abstract</b> <p>A processable poly(hydroxy acid) composition which has been stabilized by adding to the polymer during the melt processing stage 0.05-3 % by weight of a peroxy compound the degradation of which produces one or more acid radicals, and which has good melt strength and elasticity. The melt strength is high enough to produce films with conventional methods as the film blowing method.</p>			

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## Processable poly(hydroxy acids)

This invention relates to poly(hydroxy acid) compositions which have high melt strength and are processable. Especially the invention relates to the use of those compositions in  
5 making films.

Biodegradable polymers, biopolymers, constitute a group of materials subject to continual development. Among them are poly(hydroxy acids) which are polymers in which monomers contain both a carboxyl group and a hydroxyl group. Examples of such polymers  
10 include polylactic acid (polylactide, PLA), poly(hydroxybutyrate), polyglycolide, and poly( $\epsilon$ -caprolactone). Polylactide or polylactic acid, which is most often prepared from lactic acid dimer, lactide, has already for years been used for medical applications like sutures, degradable bone nails or for controlled release of drugs. The molar mass of the polymer in those applications is typically very high and the polymer is purified by  
15 dissolving and precipitating it before processing, the thermal degradation is then less. The high price of the polymer and its thermal degradation during processing has limited its use in bulk applications like packaging. It has not been economically profitable to produce and handle the polymer by methods such as those used for medical applications.

20 Polylactic acid can be produced directly by polycondensation reactions, which are typical in manufacturing of polyesters. However, the highest molar masses are achieved by ring opening polymerisation of lactide. Polylactide is a thermoplastic polyester, which has properties similar to many conventional polymers. However the problem has been that these polymers are difficult to process, and for instance the producing of blown films has  
25 not been possible.

The use of polylactides also for other than medical applications has been of special interest lately. A biodegradable, compostable material for hygiene products, agricultural films and packaging applications, either for paper coatings or free films, has been sought.  
30 The reason has been both an aim towards using natural materials instead of fossil raw materials and the good mechanical and barrier properties of polylactides compared to e.g. starch based thermoplastic materials.

Polylactide is a thermoplastic polyester which resembles many conventional polymers.

There is, however, the problem that polymers break down during processing and the molar mass drops considerably. As a result, the useful life of the end products and, partly, their mechanical properties deteriorate. With conventional polymers these problems can be eliminated by using stabilizers. The aim in the use of stabilizers is to maintain the  
5 molar mass as constant as possible after polymerization, and in particular also during processing. The change in the molar mass can be monitored by means of, for example, melt viscosity.

Conventional stabilizers, which can be used with aromatic polyesters, are not effective on  
10 lactic acid polymers. Boric acid, which, according to German patent application DE 4102170, is used for the stabilization of poly(hydroxybutyrate), does not function with lactic acid polymers.

Certain experiments on various stabilizers have been published. In Japanese patent  
15 publication JP68008614, polylactic acids have been stabilized with lactone compounds, such as  $\gamma$ -butyrolactone or  $\alpha$ -acetal- $\gamma$ -butyrolactone. Japanese patent publication JP68002949 describes the adding of isocyanate to improve the heat resistance of lactic acid polymer. These methods have been experimented with, but the results have remained  
20 poor.

Attempts have also been made to produce films from pure polylactides, but with no success. Some films have been made by blending with other polymers or from copolymers.

25 In the German patent application DE 43 00 420 there has been given a blend of polylactide and another aliphatic polyester, preferably polycaprolactone. The polymers are mixed in the melt, granulated and the granules are treated for extended times at temperatures just below melting in order to achieve a transesterification.

30 The PCT-application WO 92/04493 disclose polylactide compositions with high amount of lactide or lactide oligomers as plasticizing agents in order to achieve flexibility.

In the PCT-application WO 94/07941 melt stable polylactide compositions have been

given which are said to be suitable for films. The residual lactide and moisture content have to be very low, and a certain amount of mesolactide must be used in the polymerization. Some "films" are prepared in the example 2 by extrusion of thick sheets. The thicknesses of the tested products is 1-13 mm. Test bars are used in all other examples.

- 5 Also according to this patent application it is most preferable to use polylactide blends with e.g. polycaprolactone.

Poly lactides or copolymers have been made into self-supporting films by casting from solutions or by pressing, as are given already in very old patent publications. As examples  
10 are US 2 703 316 and US 4 045 418.

- It is obvious that although many attempts to make films have been made, large scale production based on economical conventional large-scale blown film methods to make thin oriented films has not been possible due to low or missing melt strength of the polymer.  
15 If films have been obtained with some method they have been brittle and have had very low elongation at break values unless heavily loaded with plasticizers or blended with other polymeric components.

- An other important issue is melt stability. It is well known that poly lactides degrade at elevated temperatures during melt processing. Although most mechanical properties would  
20 be retained above a certain threshold molar mass, the viscosity decreases drastically and also this makes film blowing of these polymers impossible. Only in the already above mentioned PCT application WO 94/07941 melt stable compositions have been discussed, but even here the melt strength is not sufficient for film blowing. The melt stability  
25 in that publication is a sum of many different factors and a certain strictly defined polymer composition is needed.

- According to the present invention, it has now been observed, surprisingly, that polylactic acids can be stabilized by adding various peroxides to the mixture during processing or as  
30 a separate step. By peroxide addition, the scission of chains can be reduced, i.e. the decrease in molar mass can be slowed down. The stabilizing effect of peroxides can also be observed from the melt viscosity value, which, owing to the peroxide addition, decreases during processing considerably more slowly than without peroxide. The effect of peroxi-

des can be manyfold. The catalyst deactivation and end group capping seem to be possible mechanisms. Crosslinking can be neglected, because no gel formation can be observed. The theoretical background of the action of peroxides is outside the scope of this invention.

5

Further, the object of this invention is to achieve a polylactide composition, which has good melt strength and elongation. Further an object has been to achieve a composition which possesses a melt strength high enough for making films by conventional processing methods, especially by film blowing methods.

10

In stabilization according to the invention it is possible to use a number of commercially available organic peroxy compounds. Especially suitable are peroxy compounds from which acids are formed as degradation products. It is evident that this acid radical stabilizes the hydroxyl end group of the polymer. Furthermore, it has been observed that  
15 peroxides acting as stabilizers are characterized by a short half-life, preferably below 10 s, but most preferably below 5 s. Examples which can be given of suitable peroxides include dilauroyl peroxide (half-life at 200 °C 0.057 s), tert-butylperoxy-diethylacetate (0.452 s), t-butylperoxy-2-ethylhexanoate (0.278 s), tert-butylperoxyisobutyrate (0.463 s) and tert-butylperoxyacetate (3.9 s), tert-butylperoxybenzoate (4.47 s) and dibenzoylperoxide  
20 (0.742 s). The last-mentioned two have proved to function especially well. It is natural that only a few examples of functioning peroxides were mentioned above, and that other peroxides functioning in a corresponding manner are also within the scope of the invention.

25 The amount of peroxide used is preferably 0.01-3 % by weight. The most preferable amount depends on the peroxy compound.

Surprisingly it has also been found that by stabilising polylactides with certain peroxides the melt strength and elongation after stabilization are very high. The elongation is even  
30 150-300 %. This enables the film blowing of polylactides using conventional commercial film blowing equipment. The films can also be effectively oriented.

The polylactide used can be made from L-, D- or D,L-lactide or their blends with any

polymerization method. Also copolymers or polymer blends can be used, but it is not necessary for the usability of the invention. Especially preferable it is to use poly-L-lactide. The polymer according to the invention has a weight average molecular weight ( $M_w$ ) of about 20 000 - 400 000, preferably 40 000 - 200 000. This relates to a number  
5 average molecular weight ( $M_n$ ) of 10 000 - 200 000, preferably 10 000 - 100 000.

Poly lactide films can easily be tailored to different purposes by adding small amounts of conventional plasticizers, pigments, fillers etc.

10 Suitable plasticizers are generally available commercial plasticizers like di- or tricarboxylic acid esters, epoxide oils or esters, polymeric polyesters, aliphatic diesters, alkylether mono- or -diesters and glycerine esters. Also blends of these plasticizers can be used. If plasticizers are used, the suitable amounts are 0.5-30 weight-%.

15 As fillers all conventional inorganic or organic fillers can be used, like calcium carbonate, kaolin, mica, talc, silicium oxide, zeolite, glass fibers or spheres, starch or saw dust. Suitable amount of filler can be 0.5-50 weight-% depending on the end product.

Films can be made by film blowing methods from the polylactide composition according  
20 to this invention, which is one of the biggest benefits of this invention. In addition to that, of course, cast films or sheets can be made, which does not usually set as high demands on the material. The thickness of the blown or cast films can easily be tailored according to the end product by using polymers with different molar masses and by varying the amount of peroxides and also by adding suitable plasticizers and/or fillers.

25 The objects of usage of the films are all conventional applications of films and especially those where one wants to minimize the amounts of waste and to treat for instance by composting. Such applications are e.g. different packaging materials like pouches, films, bags and hygiene products like diapers and different agricultural films.

30 Sheets made from polylactide can be processed to different packaging trays or lids, or in agricultural use to shallow containers or pots.

Many different kinds of products can be made from the polymer composition according to this invention. One such application is so called twist-films, which means for example wrappings used for candies, which are wrapped around the product and twisted in both ends to close the package. The twist should remain closed and not open before the candy  
5 is used by the consumer. Not many polymers exist which have good twist properties. One of the best twist materials has been cellophane.

It is also typical for the films and sheets made from the polymer composition according to the invention that they are easily sealable either by heat sealing or high frequency  
10 sealing. Also different printing inks, also water soluble, stick to the film very well.

The invention is described in greater detail with the help of the following examples.

In the examples 1-3, two different poly(L-lactic acids) were used, having their weight-  
15 average molar masses  $M_w$  were 160,000 and respectively 140,000 g/mol, and their number-average molar masses  $M_n$  were approximately 70,000 and respectively 60,000 g/mol. Thus the ratio of the molar masses  $M_w/M_n$  was approximately 2.3. The polymers were prepared at Neste Oy and were used as such in the experiments. The following peroxides were used for stabilization in the experiments:

- 20 A. dibenzoyl peroxide (Fluka), half-life 0.742 s
- B. di-tert-butyl peroxide (AKZO), half-life 20.5 s
- C. dicumyl peroxide (AKZO), half-life 14.7 s
- D. tert-butyl peroxybenzoate (AKZO), half-life 4.47 s

25 All of the peroxides were commercial products and were used as such.

In other examples also polylactides produced by Neste Oy having molar masses ( $M_n$ ) of 115 000, 130 000 ja 145 000 were used.

30 The molar masses were determined with GPC (Gel Permeation Chromatography) equipment by using the polystyrene standard. DSC (Differential Scanning Calorimetry) measurements were performed with Perkin Elmer DSC 7 and Mettler DSC-30S equipment. The weight of the samples in these measurements was 10 mg. The heating and



cooling rate was 10 °C/min, and there were two cycles in the measurements. The thermogravimetric analyses (TGA) were performed by using a Mettler TG50 device. The sample size in the measurements was 10 mg, the sample was heated in a nitrogen atmosphere to 500 °C, and the heating rate was 10 °C/min. The gel content of the polymer was determined according to the method ASTM D 2765 by using chloroform as the solvent.

#### Example 1. Films

- 10 The stabilization of polylactic acid was investigated by using a Brabender mixer (Plasticorder<sup>®</sup>PL 2000), by means of which it was possible also directly to monitor the melt viscosity of the compound from the torque of the machine. 40 g of polylactide having  $M_w$  160.000 was mixed with 0-3 % of dibenzoyl peroxide (A) for 5 min at 180 °C. It was assumed that all the peroxide had reacted, and DSC measurements showed no extra peak.
- 15 The polymer samples were compressed between PET films for 15 s, at a pressure of 200 bar and a temperature of 180 °C. After molding, the films were cooled rapidly to room temperature. The thickness of the film was 250-300  $\mu$ m. The film dissolved in chloroform, and no gel was optically detectable.
- 20 The amount of peroxide added affected the melt viscosity, as can be seen from Figure 1. Melt viscosity increases when peroxide is added in an amount of 0-0.5 % by weight, but the difference is small between an addition of 0.5 % by weight and 3.0 % by weight. If no peroxide is used, the melt viscosity decreases sharply during processing.

#### 25 Example 2. Tapes

- Poly lactide having  $M_w$  140.000 was mixed with peroxides A-D. The peroxides were dissolved in a small amount of cyclohexane before being added. However, when peroxide A was used, toluene was used as the solvent, since peroxide A does not dissolve in cyclohexane.
- 30 The solvent was evaporated out from the polymer before processing. All of the experiments were carried out in a nitrogen flow. The size of the experimental batch was 40 g of polylactic acid. Thereafter the sample was processed into tapes in a Brabender Plasticorder<sup>®</sup>PL E651 single-screw extruder. The zone temperatures were 190 °C,

200 °C, 200 °C, and the nozzle temperature was 200 °C. The rotation speed of the screw was 50 rpm. The retention time in the extruder was approximately 1.5 min.

The molar mass  $M_w$  of the unstabilized reference sample of polylactide dropped during processing at least to one third of its original value.  $M_w/M_n$  dropped from the initial value 2.3 to approximately 1.9. According to DSC analysis, the reference sample had a glass transition point  $T_g$  of approximately 50 °C, a melting point  $T_m$  of approximately 170 °C, and a crystallinity  $C_r$  of approximately 50 %. According to thermogravimetric analysis, its degradation temperature ( $T_D$ ) was approximately 303 °C. Table 1 shows the molecular weights when different peroxides were used, and Table 2 shows the DSC/TGA measurement results of the corresponding experiments. The results in Table 1 show that the desired stabilization effect is not achieved with peroxides B and C, but with peroxides A and D the molar mass decreases only slightly.

Table 1. GPC measurements: PLLA N35 + peroxide A-D.

Peroxide	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_v$ (g/mol)	$\bar{M}_w/\bar{M}_n$
reference	24930	48490	45190	1,95
A 0,1 wt-%	44250	98800	90600	2,25
A 0,5 wt-%	52650	107000	98050	2,05
A 0,7 wt-%	56200	109500	100250	1,95
A 1,0 wt-%	56600	115000	105000	2,00
B 0,1 wt-%	17100	32850	30650	1,90
B 0,5 wt-%	14750	27550	25750	1,85
C 0,1 wt-%	16950	32400	30250	1,90
C 0,5 wt-%	15450	31750	29500	2,10
D 0,1 wt-%	38200	80300	73850	2,10
D 0,2 wt-%	48450	115500	105000	2,40
D 0,5 wt-%	43900	92650	84300	2,05
D 0,7 wt-%	55250	127000	114500	2,30
D 1,0 wt-%	41600	95950	85300	2,30
D 3,0 wt-%	30200	121000	97900	4,00

Table 2. DSC/TGA measurements: PLLA N35 + peroxide A-D.

Peroxide	T <sub>g</sub> (°C)		T <sub>m</sub> (°C)		$\Delta H_m$ (J/g)		C <sub>r</sub> (%)	T <sub>D</sub> (°C)
	I	II	I	II	I	II	$\Delta H_{100\%} = 93,6 \text{ J/g}$	
reference	42,6	49,6	168,1	169,8	41,5	46,9	50,1	303
A 0,1 wt-%	50,1	50,2	165,5	172,7	32,3	33,5	35,8	315
A 0,5 wt-%	-	47,9	160,4	171,8	33,9	36,2	38,7	313
A 0,7 wt-%	-	49,8	155,6	172,7	30,7	37,9	40,5	313
A 1,0 wt-%	-	41,0	162,4	168,4	34,7	39,4	42,1	313
B 0,1 wt-%	33,6	45,1	164,4	166,9	41,4	46,3	49,5	305
B 0,5 wt-%	33,6	46,3	163,2	166,7	41,8	45,6	48,7	303
C 0,1 wt-%	34,0	47,8	164,4	168,5	41,7	46,2	49,4	307
C 0,5 wt-%	34,3	46,5	163,1	166,6	41,0	43,8	46,8	309
D 0,1 wt-%	35,2	48,2	165,3	170,2	36,0	37,5	40,1	313
D 0,2 wt-%	39,5	49,5	165,3	171,8	33,2	33,9	36,2	313
D 0,5 wt-%	33,9	46,5	164,3	168,6	34,1	36,1	38,6	315
D 0,7 wt-%	30,6	44,5	164,4	170,3	34,3	40,7	43,5	317
D 1,0 wt-%	32,4	45,6	162,3	165,1	33,8	35,6	38,0	319
D 3,0 wt-%	34,1	47,6	155,3	161,8	28,5	31,2	33,3	321

I = first heating 200 °C (10 °C/min);

II = second heating 200 °C (10 °C/min).

### Example 3. Gel formation

The possible crosslinking of polylactide was investigated by measuring the gel content of the polymer after the peroxide treatment. Polylactide was blended with different amounts of dibenzoyl peroxide by the method described in Example 1. The gel content was measured according to ASTM D 2765, but chloroform was used instead of xylene. No gel formation was observed if peroxide content was below 0.25 weight-% and even with peroxide content 3 weight-% the gel formation was low. When the results were further investigated with a particle size analyzer Malvern 2600c, it could be seen that the amount of very small particles was dominating with lower peroxide contents and the amount of large particles was increasing with increasing peroxide amounts. The results are given in

Table 3.

Table 3

5	added peroxide wt-%	gel con- tent %	particle size 1,9-10 $\mu\text{m}$ %	particle size 10-50 $\mu\text{m}$ %	particle size 50-100 $\mu\text{m}$ %	particle size 100-190 $\mu\text{m}$ %
	0	0	0	0	0	0
	0.1	0	0	0	0	0
10	0.25	0.9	86.0	13.0	0.2	0.8
	0.50	1.8	50.0	31.0	3.7	15.5
	3.00	5.1	0.2	1.3	5.1	93.4

#### 15 Example 4. Melt properties of stabilized polylactides

Poly-L-lactide (PLLA) was stabilized according to the method described in the previous examples which means that the polymer was melt mixed with dibenzoylperoxide (Fluka, half-life 0.742 s) for 5 min at 180 °C. The equipment used to measure the melt properties was a Göttfert extruder, screw diameter 30 mm and length 20 D, provided with a melt pump and capillar die, L/D = 100/3. The take-off unit was a Göttfert Rheotens tester for uniaxial extension of polymer melts. The polymer melt strand was gripped between two corotating wheels which elongate the strand with constant velocity or constant acceleration until the strand breaks. The constant acceleration was used in this experiment. The tensile force used to elongate the polymer melt was recorded as a function of the speed of the elongated strand.

The temperature profile of the extruder was 160-180-180-180 and the temperature in the melt pump and die was 180 °C. The die pressure was adjusted by the melt pump rpm to

avoid melt fracture in the polymer strand. The tensile force of the melt at different speeds is given in Table 4. The stabilized polylactide was compared to unstabilized polylactide and also to a film grade low density polyethylene with melt index 4.5.

5 **Table 4. Tensile force of the melt, cN**

speed mm/s	PLLA 0.1 % stab	PLLA 0.2 % stab	PLLA 0.5 % stab	PLLA	LDPE MI 4.5
60	0.7	0.7	5.3	0	3.3
120	1.3	1.4	8.3	0	8.3
180	2.3	2.3	10.0	0	10.7
300	2.7	3.3	11.0	*	12.7
600	3.0	4.0	12.7	-	14.3
at break	-	-	13.0/660	-	15.0/750
1200	3.0	4.0	-	-	-

15 \* No detectable force was recorded during the measurement and at higher speed the melt stuck to the wheels stopping the rotation

From the results it can be seen that polylactide stabilized with 0.5 % peroxide is comparable with film grade polyethylene.

20

#### **Example 5. Melt strength properties of stabilized polylactides**

Blown films of different grades of polylactide were produced by a Brabender extruder, screw diameter of which was 19 mm and length 25 D. The extruder was provided with a blow film die of 25 mm in diameter and 1.0 mm die gap. The temperature profile in the extruder was set to 170-180-190 °C and to 190 °C in the die. The screw speed was set at 30 rpm. The blow-up ratio was 2:1. The thickness of the film varied from 10 µm to 150 µm and was adjusted by the speed of the take-off unit.

The extrusion process was followed by a visual inspection of the bubble stability which is the main criteria of proper film blowing and corresponds to the melt strength and elasticity of the polymer extruded. Steady state extrusion was held for one hour.

- 5 The film extrusion properties of stabilized and unstabilized polylactides with different molar masses are given in table 5. No blown films could be made from unstabilized polylactide. From the results it can be seen that suitable stabilizer amounts are bigger for polylactides having lower molar masses in order to make proper blown films.
- 10 From the examples 4 and 5 it can clearly be seen that the polylactide composition can effectively be tailored for different film applications from thin films to thick ones by changing the molar mass of the polymer and the amount of stabilizer.

**Table 5.**

15

$M_w$	stabilizer by weight	Bubble properties
145 000 (polym A)	none 0.1 % 0.2 %	Bubble collapses due to too low melt strength Very good bubble stability at thin gauges 10-50 $\mu\text{m}$ Very good stability at thicker gauges around 100 $\mu\text{m}$
130 000 (polym B)	none 0.1 % 0.2 %	Bubble collapses due to too low melt strength Good bubble stability at thin gauges of 10-50 $\mu\text{m}$ Very good stability at thin gauges
115 000 (polym C)	none 0.1 % 0.2 % 0.5 %	Bubble collapses due to too low melt strength Bubble unstable, some bubbles break Bubble unstable, no breaks Good stability at thinner gauges of 10-50 $\mu\text{m}$

20

25

**Example 6. Physical properties of blown film of stabilized polylactide compared to unstabilized polylactide**

As described above blown film of unstabilized polylactide cannot be made due to lack of melt strength of the polymer. It is however possible to produce blown film of unstabilized blown film by coextrusion. A coextrusion film was made in which the polylactide layer is between two layers of polyethylene, the die temperature setting was 190 °C. The used polyethylene was film grade LDPE, NCPE 4024 produced by Borealis Polymers Oy with a melt index of 4,0. The polylactide film was peeled off from the polyethylene layer which is possible because of the relatively low adhesion between polylactide and polyethylene.

Coextrusion films can of course be made also from stabilized polylactides. It might in some special cases be a good method if aseptic film is needed for a special purpose.

The physical properties of the stabilized and unstabilized polylactide films are given in Table 6.

**Table 6**

sample	stress at peak, MPa	elongation at break, %
A + 0.1 % stab.	MD 41 TD 34	MD 290 TD 220
B + 0.2 % stab.	MD 31 TD 30	MD 225 TD 194
A + PE	MD 46 TD 38	MD 5 TD 2

Polymer A:  $M_w = 145\ 000$

Polymer B:  $M_w = 130\ 000$

MD = Machine direction



TD = Transverse direction

The high flexibility of the films produced from the stabilized polylactide can clearly be seen from the results.

5

#### Example 7. Addition of plasticizers to stabilized polylactide

The films made from stabilized polylactide are already flexible as such, but can still be further tailored by adding plasticizers to the polymer. A commercial stabilizer was used  
10 in the experiments: Emuldan SHR 60, which is a blend of glycerolmonooleate and dioleate (producer Grindsted Products AS, Denmark).

Films were made as described in example 5.

15 The stress at peak and elongation at break have been given in Table 7. From the results it can be seen that by adding plasticizers the film properties can be further improved and especially the properties in machine direction and transverse direction become more even.

Table 7

20

sample	stress at peak, MPa	elongation at break, %
A + 0.1 % stab.	MD 41 TD 34	MD 290 TD 220
A + 0.1 % stab + 5 % Emuldan	MD 34 TD 30	MD 290 TD 270
25 B + 0.2 % stab.	MD 31 TD 30	MD 225 TD 194
B + 0.2 % stab. + 2 % Emuldan	MD 41 TD 39	MD 260 TD 250

Sample A:  $M_w = 145\ 000$

Sample B:  $M_w = 130\ 000$

MD = Machine direction

TD = Transverse direction

5

#### Example 8. Addition of fillers to polylactide

Different amounts of commercial fillers were added to the stabilized polylactide compositions. Fillers and plasticizers can also be used together.

10

Films were produced according to the procedure described in Example 5. Results are given in Table 8. From the results it can be seen that a small amount of talc gives a very strong and stiff film whereas with greater amounts of kaolin a soft film is obtained which can be further softened by small amounts of some plasticizer.

15

**Table 8**

20

25

sample	stress at peak, MPa	elongation at break, %
B + 0.2 % stab.	MD 31 TD 30	MD 225 TD 190
B + 0.2 % stab + 10 % talc	MD 47 TD 38	MD 120 TD 8
B + 0.2 % stab. + 30 % kaolin	MD 28	MD 190
B + 0.2 % stab. + 2 % Emuldan + 30 % kaolin	MD 12 TD 10	MD 210 TD 90

Sample B:  $M_w = 130\ 000$

MD = Machine direction

TD = Transverse direction

**Example 9. Twist properties of stabilized polylactide films**

- 5 When packing of for instance candies in individual wraps they are closed in both ends by twisting about one and half turn. Because one of the best twist materials is cellophane, the comparative test was made using it. The twist properties of the polylactide composition according to the invention were very good.
- 10 Twist properties were tested with an equipment developed in-house where the film is covered around the candy surrogate and twisted 1.6 turns in both ends. The machine measures the force needed to open the twist and also the angle which the twist opens by itself. The results for polylactide and cellophane are given in Table 9.

15 **Table 9.**

sample	return angle, °	opening force, N
A + 1 % stab.	55 - 60	5 - 6.5
cellophane	130 - 190	4 - 5

20

**Example 10. Sealability and printability of polylactide films**

- The sealing properties of the films made in example 6 were investigated. The sealability  
25 of the films was good. Heat sealing was done at 105 °C, sealing time was 0.5 seconds. Only one sealing bar was heated during sealing. High frequency sealing was made at 60 °C. Seals were complete in both cases.

- The printability of the films was tested and films were found to be printable without  
30 corona treatment with both solvent and water based inks. The print had very good adhesion to the film as tested by the tape method.

**Example 11. Degradation of polylactides buried in soil**

To show that stabilized polylactides biodegrade at least as well as nonstabilized, test bars with different levels of stabilizers were made by injection molding. The specimens were buried in soil and they were removed at certain time intervals to be tested for mechanical properties. The results have been collected in Table 10 and from them it can be seen that all samples became brittle after 6-8 weeks.

**Table 10.**

sample	time, weeks	tensile modulus MPa	tensile strength MPa	stress at break MPa	elongation at break %
A	0	3250	56.2	41.3	3.55
	2	2160	44.0	27.3	18.00
	4	1850	26.3	26.3	1.53
	6	-	-	-	-
	8	225	0.8	0.8	0.42
A + 0,1 % stab	0	2230	47.2	28.9	7.47
	2	1590	32.7	18.3	47.40
	4	1949	10.7	10.6	0.50
	6	-	-	-	-
	8	284	1.1	1.1	0.41
A + 0,25 % stab	0	2190	47.4	34.3	5.08
	2	1610	28.3	28.2	2.48
	4	614	3.4	3.4	0.64
	6	398	1.5	1.5	0.43
	8	271	0.9	0.9	0.36
A + 0,5 % stab	0	1630	39.8	13.5	219.00
	2	1550	29.6	27.5	5.83
	4	1050	3.0	3.0	0.32
	6	362	1.3	1.3	0.44
	8	197	0.7	0.7	0.37

**Example 12. Degradation of stabilized polylactide products at constant humidity**

Test bars according to Example 11 were also stored at constant conditions, temperature

23 °C and humidity 50 %. This was done to check the hypothesis that the first stage in biodegradation is hydrolysis by water. The mechanical properties are given in Table 11. Also the molar masses were measured, results are in Table 12. According to the results the hydrolysis rate is higher for the stabilized samples than for nonstabilized. That is

5 probably due to a different crystal structure.

Table 11.

	sample	time, weeks	stress at yield MPa	tensile strength MPa	stress at break MPa	elongation at break %
10	A	0	3250	56.2	41.3	3.55
		2	2950	51.6	33.8	4.65
		4	2800	50.4	31.9	5.10
		6	2220	45.4	30.9	5.73
15	A + 0.1 % stab	0	2230	47.2	28.9	7.47
		2	1150	26.0	17.2	362
		4	1210	16.3	15.6	355
		6	888	16.0	16.0	278
	A + 0.25 % stab	0	2190	47.4	34.3	5.08
		2	1260	25.3	16.6	344
		4	1170	17.3	15.4	335
		6	910	16.9	16.8	276
	A + 0.5 % stab	0	1630	39.8	13.5	219
		2	1280	19.0	15.3	324
		4	1110	14.2	14.2	316
		6	745	16.2	16.1	251

Table 12

	time weeks	Polym. A	Polym A + 0.1 % stabil.	Polym A + 0.25 % stabil.	Polym A + 0.5 % stabil.
$M_w$ g/mol	0	77000	117000	125000	150000
	1	77000	105000	104000	118000
	4	75000	58000	68000	75000

5

As can be seen from the above examples, polylactide compositions with good melt strength and the possibility to produce them, enables their use for a great variety of different applications.

## Claims:

1. A processable poly(hydroxy acid) composition having a number average molecular weight of at least 10.000, characterized in that the melt strength and elasticity of the polymer have been achieved by reactive extrusion of poly(hydroxy acid) with an organic peroxide.
2. A polymer composition according to claim 1 characterized in that during the melt processing step there is added to the polymer, in an amount of 0.05-3 % by weight, an organic peroxide compound the degradation of which produces one or several acid radicals.
3. A polymer composition according to claim 1 or 2 characterized in that the the number average molecular weight of poly(hydroxy acid) is 10.000-200.000.
4. A polymer composition according to claims 1-3 characterized in that the amount of peroxides is 0.05-0.8 weigth-% of the amount of polymer.
5. A polymer composition according to claims 1-4 characterized in that the half-life of the peroxide used is below 10 s at a temperature of 200 °C.
6. A polymer composition according to claims 1-5 characterized in that the peroxide is tert-butylperoxybenzoate or dibenzoylperoxide.
7. A polymer composition according to claims 1-6 characterized in that the poly(hydroxy acid) is poly-L-lactide.
8. A polymer composition according to any of the preceding claims characterized in that the melt strength and elasticity are suitable for manufacturing blown films.
9. A polymer composition according to any of the preceding claims characterized in that the melt strength and elasticity are suitable for manufacturing cast films or sheets.

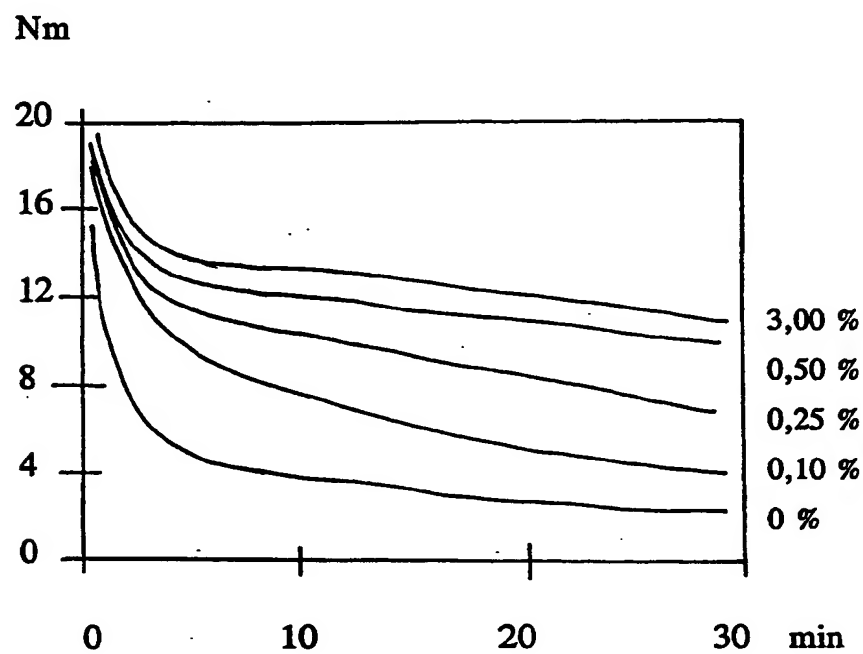
10. A polymer composition according to any of the preceding claims characterized in that it contains 0.5-30 weight-% plasticizer.
11. A polymer composition according to claim 10 characterized in that the plasticizer is  
5 chosen from the group consisting of di- and tricarboxylic acid esters, epoxy oils and esters, polymeric polyesters, aliphatic diesters, alkylethermono and diesters and glycerine esters or mixtures thereof.
12. A polymer composition according to any of the preceding claims characterized in that  
10 it contains 0.1-50 weight-% filler.
13. A polymer composition according to claim 12 characterized in that the filler is chosen from the group consisting of calcium carbonate, kaolin, mica, talc, silicium dioxide, zeolite, glass fibers or spheres, starch or sawdust.  
15
14. Films or sheets made from a polymer composition according to any of claims 1-13.
15. Films according to claim 14 manufactured by film blowing extrusion.
- 20 16. Films or sheets according to claim 14 manufactured by cast extrusion.
17. Films or sheets according to any of the claims 14-16 characterized in that they are sealable by heat or high frequency sealing.
- 25 18. Films or sheets according to any of the claims 14-16 characterized in that they are printable with solvent or water based inks.
19. Films or sheets according to any of the claims 14-18 characterized in that they have good twist properties.  
30
20. Use of films according to claims 14-19 in hygiene products like diapers, agricultural films, packaging materials like bags, pouches, shrink or twist film packages.



21. Use of sheets according to claims 14-19 in thermoformed packaging articles like trays or lids and agricultural products as cultivation trays or pots.

22. Films, sheets and products according to any of the claims 14-21 **characterized** in that  
5 they are hydrolysable and biodegradable.

1/1

*Fig. 1*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00586

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08G 63/08, C08G 63/88, C08L 67/04, C08J 5/18, C08K 5/14  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08G, C08J, C08L, C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA, REGISTRY FILE, WPI, CLAIMS, EPODOC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	Polymer Degradation and Stability, Volume 46, 1994, A. Södergård et al, "Stabilization of Poly (L-lactide) in the melt" page 25 - page 30 --	1-22
P,A	WO, A1, 9407949 (CARGILL, INCORPORATED), 14 April 1994 (14.04.94) --	1-22
A	US, A, 3523920 (HERMAN S. SCHULTZ), 11 August 1970 (11.08.70) -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

3 April 1995

Date of mailing of the international search report

13 -04- 1995

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

25/02/95

International application No.

PCT/FI 94/00586

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9407949	14/04/94	NONE	
US-A- 3523920	11/08/70	DE-A- 1928102 GB-A- 1275082	11/12/69 24/05/72

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